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(54) **Superconducting ceramics and methods for manufacturing the same.**

(57) A superconducting coil or otherwise patterned superconductor is formed by sputtering onto a substrate surface a layer of a material of the same chemical composition as a known high Tc ceramic superconductor and subsequently selectively irradiating the layer with a laser beam so as to define irradiated and non-irradiated regions. The sputtered layer is disordered and has many lattice defects and imperfections and thus is basically non-superconducting, but by irradiation with a laser beam the sputtered layer is melted and then recrystallizes into an ordered and superconducting material. By tracing the laser beam across the surface of the sputtered layer desired superconducting conductor patterns (e.g. coil windings) are readily obtained. Multiple layers can be successively deposited and irradiated to form multilayer superconducting devices useful, for example, as superconducting coils.

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Description

Superconducting Ceramics and Methods for Manufacturing the Same

BACKGROUND OF THE INVENTION

This invention relates to superconducting ceramics and methods for manufacturing the same.

It has been known to use metallic materials such as Nb3Ge to wind a coil to form a superconducting magnet since such metallic materials have a high ductility and malleability. However such metallic materials do not have a high Tc, and in recent years, superconducting ceramics which have a high Tc have attracted the interest of researchers. However, such superconducting ceramics are fragile and have low ductility and malleability, and therefore it has been quite impossible to form a superconducting coil from a conductor made of such superconducting ceramics.

OBJECTS AND SUMMARY OF THE INVENTION

It is therefore the object of the present invention to provide a high Tc superconductor in any desired form and to provide a method of manufacturing a high Tc superconductor in any desired form, which method is suitable for mass-production.

The present invention resides generally in the concept of providing a layer of a prescribed material on a substrate and irradiating the said layer so as, depending upon the original properties of the layer, either to convert it into a superconducting layer in the regions where it is irradiated or to convert it from a superconducting layer in the said regions. The invention takes advantage of the fact that the superconductivity of a material is not only dependent upon its chemical composition but also is dependent upon the orderliness of its structure, and proposes either to render an ordered superconducting structure into a disordered non-superconducting structure or vice-versa by irradiation. Furthermore, by selectively irradiating only specific regions of a structure high Tc superconductors can be formed into coils and other shapes which have hitherto been unobtainable.

In accordance with an embodiment of the present invention which is described hereinafter, an oxide mixture prescribed for constituting a superconducting ceramic is first deposited in the form of a thin film onto a substrate by sputtering. By making use of sputtering to form the thin film, an amorphous or other structure of the resultant film is obtained which is abundant in lattice defects and/or imperfections so that the resistivity of the ceramic material is rather high. Prescribed portions of the thin film are then irradiated with a laser beam which, for example, scans the surface of the ceramic layer within a constant width, strip-shaped region of the layer. The irradiated portion of the layer is melted and annealed by the laser and recrystallizes as it cools. By virtue of the annealing effect of the laser, the number of lattice defects and imperfections is decreased and the amount of lattice strain is decreased, so that a microcrystalline structure having superconductive properties is obtained only in the irradiated regions whereby a superconducting pattern may be obtained. The recrystallization results furthermore in impurities contained in the ceramic material being redistributed and collected near the surface of the thin film layer so that a high purity superconducting ceramic can be obtained in the thickness of the thin film.

The sputtered ceramic material may for example be such as those represented by the formulae $(Y_{1-x}Ba_x)_2CuO_4$, hereinafter called YBCO, where $x = 0.01$ to 0.1 and preferably 0.05 to 0.1, $(La_{1-x}Ba_x)_2CuO_4$, hereinafter called BLCO where $x = 0.01$ to 0.1 and preferably 0.05 to 0.1; $(La_{1-x}Sr_x)_2CuO_4$, hereinafter called SLCO, where $x = 0.01$ to 0.1 and preferably 0.05 to 0.1, and $(La_{1-x}A_x)_2CuO_4$, where A represents an element in Group IIa of the Japanese Periodic Table and where $x = 0.01$ to 0.1 and preferably 0.05 to 0.1. The irradiation of the ceramic layer may be carried out in an oxidizing atmosphere, in which case the proportions of the above composition may be decreased correspondingly so that the desired stoichiometry are obtained taking account of oxidation of the irradiated thin film portions.

Those parts of the thin film layer intervening between neighbouring superconducting portions function as insulators which isolate the superconducting portion from its surroundings and also provide the resulting superconducting device with an even upper surface which enables multi-layered structures to be formed.

This isolating effect is advantageous in view of the fact that in the prior art the characteristics of superconducting ceramics have tended to be influenced by the material which is in contact with the ceramics in the structure of the superconducting device. For instance, when a substrate made of silicon oxide or silicon nitride has been used, acid-base reactions have been known to occur between the substrate and an oxide superconducting ceramic layer formed thereon.

As will be appreciated from consideration of the following descriptions, the present invention enables superconductors to be formed in various shapes by a method which is very simple as compared to photolithography so that the present invention can be particularly effective when applied to mass-production manufacturing.

Further features of the invention are set forth with particularity in the appended claims and will become apparent to those possesssed with the relevant skills from consideration of the following description, given with reference to the accompanying drawings, of exemplary embodiments of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1(A) to 1(C) are side views illustrating a first exemplary manufacturing process in accordance with the present invention;

Figs. 2(A) to 2(C) are side views illustrating a second exemplary manufacturing process in accordance with the present invention;

Fig. 3 is a perspective view illustrating a third exemplary manufacturing process in accordance with the present invention;

Fig. 4 is a cross sectional view illustrating a fourth exemplary manufacturing process in accordance with the present invention;

Fig. 5 is a perspective view illustrating a fifth exemplary manufacturing process in accordance with the present invention;

Fig. 6 is a perspective view illustrating a sixth exemplary manufacturing process in accordance with the present invention; and

Figs. 7 and 8 are graphical diagrams showing the relationship between the resistivity and the temperature of superconducting oxide ceramics manufactured in accordance with the present invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

For the avoidance of doubt it is to be noted that all references herein and in the appended claims to the Periodic Table and to specific Groups of the Periodic Table are to be understood to refer to the Japanese Periodic Table and to the Groups thereof as described in the Iwanami "Physics and Chemistry Dictionary". As compared with the Group designations of the Periodic Table as described in "The Penguin Dictionary of Science" for example, which are the Group designations commonly accepted throughout Europe, Groups Ia, IIa, VIII, Ib, IIb and 0 are the same in the Japanese and European Periodic Tables, Groups IIIa, IVa, Va, VIa and VIIa of the Japanese Periodic Table correspond respectively to Groups IIIb, IVb, Vb, VIb and VIIb of the European Periodic Table, and Groups IIIb, IVb, Vb, VIb and VIIb of the Japanese Periodic Table correspond respectively to Groups IIIa, IVa, Va, VIa and VIIa of the European Periodic Table.

Referring to Figs. 1(A) to (C), a manufacturing process in accordance with the present invention will be described. In Fig. 1(A), a substrate 1 may be made of a ceramic material such as alumina, silicon oxide, aluminium nitride, zirconia, yttria or USZ(yttria stabilized zircon), or may be made of metal or of glass. YSZ, yttria or zirconia are particularly suitable having regard to the desirability of matching the coefficient of thermal expansion of the substrate to that of the superconducting layer formed thereon as hereinafter described. The differential coefficient of thermal expansion between the underlying substrate and the overlying ceramic thin film should be as small as possible and preferably within 50% of the thermal expansion coefficient of the ceramic thin film, since if the substrate and the ceramic thin film have substantially different thermal expansion coefficients, then strain developed between them may hinder the formation of a superconducting structure by recrystallization of the ceramic film.

A ceramic film of BLCO of 0.5 to 20 microns thickness, e.g. 2 microns, is formed on the substrate 1 by sputtering as is illustrated in Fig.1(B). The sputtering is carried out with a target mixture conforming to the formula $(La_{1-x}Ba_x)_2CuO_4$, where $x = 0.075$ for example. During the sputtering, the substrate 1 is placed in an atmosphere of argon to which a small amount of oxygen is added, and the sputtering is effected at a temperature of from room temperature to 400°C, e.g. 250°C.

Having formed the ceramic film 2 by sputtering, the next step as shown in Fig. 1(C) is to irradiate the ceramic thin film using a series of laser beam pulses 3 of 1.06 microns wavelength derived by means of a YAG laser. Each laser pulse is radiated to a circular spot described on the film which shares a 60-80% area with the irradiating spot for the preceding pulse (and also of the subsequent pulse). The laser beam is scanned across the ceramic film at a scanning speed of 2m/min. The pulse frequency is from 5 to 30 KHz, e.g. 8 KHz. The spot diameter is 50 microns. By virtue of this irradiation, the irradiated portions of the ceramic film are melted and then recrystallized. The whole substrate is heated during the laser processing to around 300-800°C, e.g. 600°C, by means of a halogen lamp. By providing this high temperature environment, it is ensured that the film does not crack as as result of too rapid cooling to room temperature from the temperature of 1300°C or higher which is momentarily experienced at the irradiated portion.

As a result of the process illustrated in Figs. 1(A) to 1(C) and described above, a superconductor is fabricated in the form of a plurality of strips 4 positioned on the film 2 with intervals therebetween. The Tc of the strips 4 was measured to be 29°C.

In a modification of the foregoing embodiment, an excimer laser (Kr, KrC1 for example) may be used instead of the YAG laser, and a strip portion of the ceramic layer of from 5-100 microns wide can be irradiated in a single operation using a linear laser beam derived by squezing with an optical system a pulsed laser beam having a 20 × 30 mm² cross-sectional area. Also, the first embodiment can be carried out making use of a pulsed laser beam emitted from an excimer laser (wavelength = 0.25 micron). In this case, the pulse frequency is chosen at about 100KHz which causes the prescribed irradiated portions of the ceramic film to be heated momentarily to about 1000°C or higher. Other manufacturing conditions for carrying out the process using an excimer laser are the same as for the process with a YAG laser. Since the power of an excimer laser is relatively high, the ceramic layer can be oxidized in an oxidizing atmosphere by the irradiation so that, for depositing the ceramic film, a sputtering target comprising $(La_{1-x}Ba_x)_2CuO_{4-d}$ may be used, where d is a compensatory factor for cancelling out the oxygen increment due to laser annealing of the ceramic in an oxidizing atmosphere, and $x = 0.075$ for example. According to experiments, conducted with the process of Figs. 1(A) to 1(C) thus a Tc of 43°K was obtained for the resultant superconductor.

Fig. 2 shows a second embodiment of the invention. In this embodiment, substantially the same procedure is repeated as for the preceding embodiment except as described below. A substrate 1 is irradiated with pulses having an elongated rectangular cross-section which are emitted from an excimer laser of 0.25 micron wavelength. The irradiation site on the substrate 1 is shifted continuously as shown in Fig. 2(C) in such a way that the

region irradiated by each pulse is superimposed on 80-98% of the preceding pulse. The scanning speed is 2cm/min. The pulse frequency is 100KHz. The beam cross-section is 50 microns thick and 10cm wide. By means of this process, a superconducting band region can be formed of 10cm width, for example.

Fig. 3 shows a third embodiment of the invention. In this embodiment, substantially the same procedure is repeated as for the first embodiment except as described below. The substrate 1 is a cylinder. On the substrate surface there is deposited a ceramic film 2 by effecting sputtering while the substrate 1 is rotating in the direction indicated by the arrow 12. After completion of the film, a laser beam irradiates the substrate. The position of impingement of the laser beam is shifted in the axial direction of the cylinder 1 while the substrate 1 is rotating around its axis. By this process, a continuous helical superconductor 4 can be formed on the cylinder 1 with each part of the helix isolated from its adjacent parts by the intervening non-superconducting ceramic film 5 which has not been irradiated.

By repeating the above process described with reference to Fig. 3, a multi-layered circuit of superconducting conductors can be constructed as is illustrated in Fig. 4 which represents a fourth embodiment of the invention. As shown in Fig. 4, a first layer 2-1 is first formed with a first superconducting helix 4-1, 4-2, ...4-n in the same manner as described above with reference to Fig. 3. Then, on top of the first layer 2-1 there is deposited a second ceramic layer 2-2, and this is followed by forming a second superconducting helix 4'-1, 4'-2, ...4'-n as above described. The end 4'-n of the second helix may be connected with the end 4-n of the first helix by means of a superconductor portion 10-1 making electrical contact with the last winding of the first helix 2-1. Since the irradiation of the second layer 2-2 also causes the upper surface of the first layer 2-1 just below the irradiated portion of the second layer to be heated and melted, therefore the second helix is formed so as not to interfere with the first helix 2-1. The forming process of the second superconducting helix 2-2 is then repeated to form third and fourth ceramic layers 2-3 and 2-4 with respective third and fourth superconducting helices which, together with the first and second helices, constitute a continuous superconductor in the form of a multilayer coil. One end portion 4'''-1 of the fourth helix is connected to a wire 30' to constitute one terminal of the coil, and the other terminal of the coil is defined by a wire 30 connected to the start end 4-1 of the first helix by way of superconducting regions of the second, third and fourth ceramic layers 2-2, 2-3 and 2-4 which are superimposed upon the end 4-1 of the first helix. If a coil having a larger number of turns is required, further ceramic layers provided with superconducting helices may be added so as to form, for example, a device comprising several tens of ceramic layers.

Although the superconducting helices are shown connected in series in Fig.4, the helices can if desired be formed without interconnections therebetween, and the superconducting patterns on the ceramic layers can be designed to produce an individual pair of terminals for each helix so that connections among the helices can be arbitrarily arranged as desired.

In Fig. 5 there is illustrated a fifth embodiment of the present invention. In this embodiment, the substrate 1 is an insulating disc which is provided with a terminal 6 at its periphery and a terminal 7 at its centre. The disc 1 is provided with a sputtered ceramic layer which is then irradiated with a laser beam in the same manner as described above for the first embodiment. During irradiation 3, the disc 1 is turned about its centre while the distance of the point of impingement of the laser beam from the centre is decreased so as to form a superconducting spiral 4 connecting the terminals 6 and 7 on the disc 1. According to experimental results that have been obtained Tc was measured to be 27°C. A multi-layered structure based upon the Fig. 5 embodiment can be constructed in a manner similar to that of the preceding embodiment, the arrangement comprising discs formed with spirals of opposed senses superposed in turn.

Fig. 6 is a perspective view showing a sixth embodiment of the present invention. In the figure, a linear laser beam 3 is shown radiated onto a disc 1 on which a ceramic film 2 is deposited having the composition of a superconducting ceramic as explained in the foregoing embodiments. During irradiation with the laser beam, the disc 1 is turned around its axis so that the ceramic film 2 is irradiated repeatedly with the laser beam and undergoes annealing and recrystallization.

Superconducting ceramics in accordance with the present invention also may be prepared in accordance with the stoichiometric formulae $(A_{1-x}B_x)_yCu_zO_w$, where A is one or more elements of Group IIIa of the Japanese Periodic Table, e.g the rare earth elements, B is one or more elements of Group IIa of the Japanese Periodic Table, e.g. the alkaline earth metals including beryllium and magnesium, and $x = 0$-1; $y = 2.0$-4.0, preferably 2.5-3.5; $z = 1.0$-4.0, preferably 1.5-3.5; and $w = 4.0$-10.0, preferably 6.0-8.0. Also, superconducting ceramics in accordance with the present invention may be prepared in accordance with the stoichiometric formulae $(A_{1-x}B_x)_yCu_zO_w$, where A is one or more elements of Group Vb of the Japanese Periodic Table such as Bi, Sb and As, B is one or more elements of Group IIa of the Japanese Periodic Table, e.g. the alkaline earth metals including beryllium and magnesium, and $x = 0.3$-1; $y = 2.0$-4.0, preferably 2.5-3.5; $z = 1.0$-4.0, preferably 1.5-3.5; and $w = 4.0$-10.0, preferably 6.0-8.0. Examples of this general formula are $BiSrCaCuCu_2O_x$ and $Bi_4Sr_3Ca_3Cu_4O_x$. Tc onset and Tco were measured for samples consistent with the formula $Bi_4Sr_yCa_3Cu_4O_x$ (y is around 1.5) and were found to be 40-60°K, which is not particularly high. Relatively high critical temperatures were obtained with samples conforming to the stoichiometric formulae $Bi_4Sr_4Ca_2Cu_4O_x$ and $Bi_2Sr_3Ca_2Cu_2O_x$. Figs. 7 and 8 are graphical diagrams showing the relationship between the resistivity and the temperature for both samples. The numbr x designating the oxygen proportion is 6-10, e.g around 8.1.

Hereinbefore, descriptions have been made of embodiments in which non-superconducting materials are converted to superconducting materials by irradiation. However, in accordance with the present invention, the inverse process is possible. Namely, a superconducting pattern can be produced by radiating a laser beam onto a superconducting thin film so that prescribed irradiated portions of the film are converted into non-superconducting material, the superconducting pattern being composed of the non-irradiated portions of the ceramic film which remain superconductive. Experiments using this inverse process were made using YBCO. After depositing a thin film of YBCO upon a substrate by sputtering, the whole film was fired at 600-900°C so as to make the film superconducting. The Tc of the superconducting film was measured and found to be 85°C. Then a prescribed portion of the superconducting film was irradiated with a laser beam at room temperature so as to convert such portion from a superconducting material to a non-superconducting material. By this process, a superconducting pattern was produced on the film in the areas thereof which had not been irradiated. An important feature of this process is that the irradiation is carried out at a relatively low temperature so that the material melted by the irradiation will be rapidly cooled and will resolidify in an agitated and disordered condition which is non-superconductive. The ambient temperature during irradiation is thus chosen to be not higher than 100°C in general. Other process conditions were the same as for the first embodiment. Of course, such an inverse process can be applied to the second to fourth embodiments in similar manner.

While the above description has been made with reference to several specific embodiments, it is to be understood that the present invention is limited only by the appended claims and is not limited to the particular examples described.

Claims

1. A method of manufacturing a ceramic material superconductor, said method comprising:

forming a non-superconducting layer on a surface, the chemical composition of said layer being substantially consistent with that of a superconducting ceramic; and

irradiating at least a portion of said layer with light so as to melt the irradiated portion and permitting the melted portion to resolidify in a superconducting configuration, the irradiation of the non-superconducting layer serving to convert the irradiated portion into a superconducting material.

2. The method of claim 1 wherein said non-superconducting layer is deposited on said surface by sputtering.

3. The method of claim 1 or 2 wherein said light is a laser beam.

4. The method of claim 3 wherein said laser beam is applied to the said layer in a sequence of pulses.

5. The method of claim 4 wherein said laser beam pulses are radiated to a portion of said layer so as to trace a line prescribed thereon.

6. The method of any preceding claim wherein said surface is constituted by the periphery of a cylinder and said light is radiated onto a helix prescribed on said layer formed on said periphery so as to form a superconducting coil.

7. The method of claim 6 wherein said cylinder is rotated about its axis during said irradiating step and the location of the impingement of said light on the said layer is shifted in the axial direction whereby the light traces a helical path on said layer.

8. The method of any of claims 1 to 5 wherein said surface is the circular surface of a disc.

9. The method of claim 8 wherein said disc is rotated during said irradiating step and the location of the impingement of said light on the said layer is shifted in the radial direction whereby the light traces a spiral path on the said layer.

10. The method of any preceding claim wherein one or more further layers of non-superconducting material are serially applied and irradiated whereby to form a multi-layered structure.

11. The method of claim 10 wherein the irradiated portions of the layers of said multi-layered structure are formed to define coils which are connected in series to form a multi-layered coil.

12. A method of manufacturing a ceramic material superconductor comprising:

forming a non-superconducting layer on a surface, the composition of said layer being so prescribed that said layer is capable of being converted to a superconducting ceramic material when irradiated, melted and recrystallized; and

irradiating and melting at least a portion of said layer with light and permitting the irradiated portion to recrystallize whereby said irradiated portion is converted from non-superconducting material to superconducting ceramic material.

13. The method of any preceding claim wherein said irradiating step is carried out under oxidizing conditions and the stoichiometric proportion of oxygen in said layer as formed is less than that of the superconducting ceramic material which is required to be produced.

14. The method of any preceding claim wherein said irradiating step is carried out at an elevated temperature of for example 300-800°C.

15. The method of claim 14 wherein said surface is heated by a halogen lamp.

16. The method of any preceding claim wherein said surface is made of YSZ, yttria or zirconia.

17. The method of claim 12 wherein said

FIG.1(A)

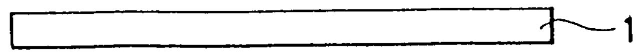


FIG.1(B)

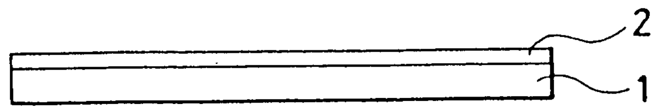


FIG.1(C)

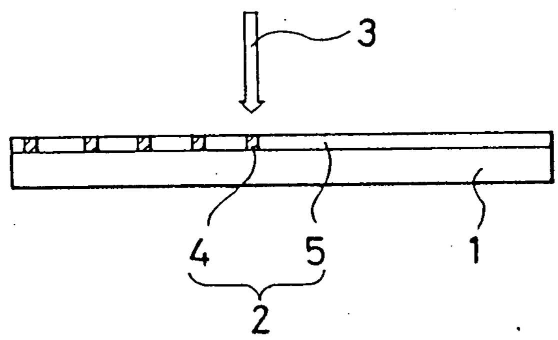


FIG.2(A)

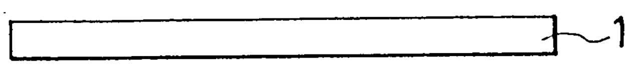


FIG.2(B)

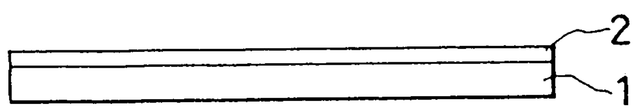


FIG.2(C)

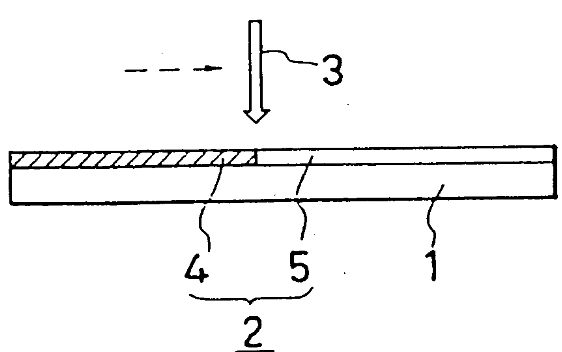


FIG.3

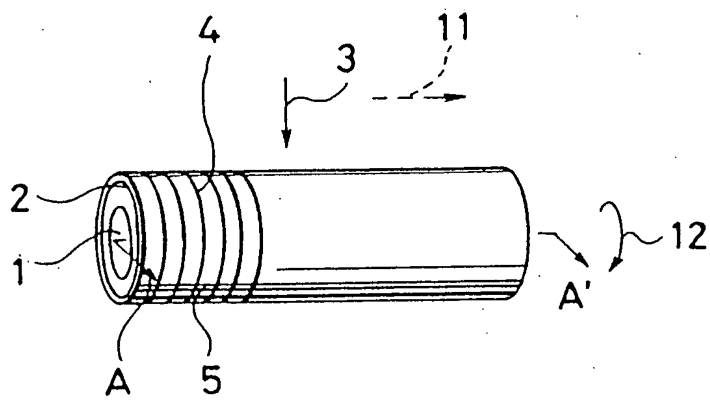
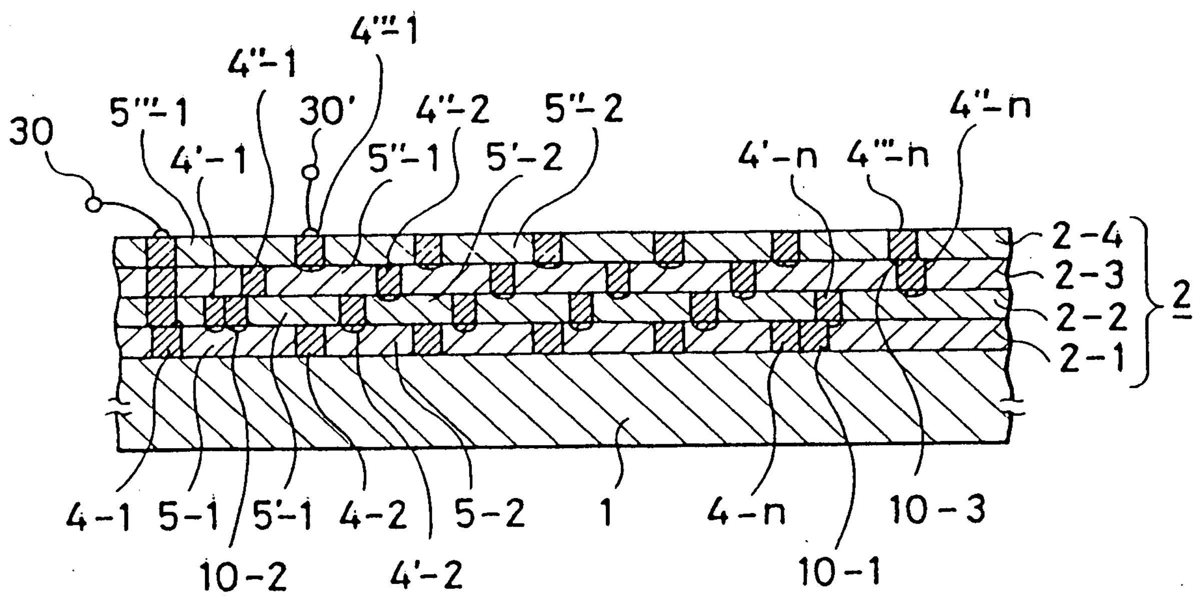

4
3
11
2
1
12
A'
A
5

FIG.4


4'''-1
4''-1
5'''-1
30'
4''-2
5''-2
4''-n
30
4'-1
5''-1
5'-2
4'-n
4'''-n
2-4
2-3
2-2
2
2-1
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4-n
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4'-2
10-1

FIG.5

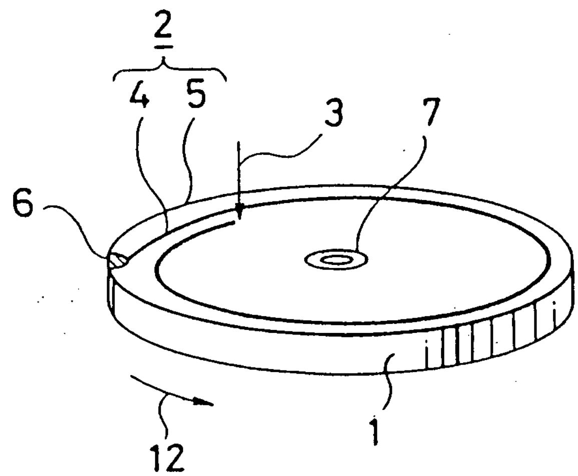

FIG.6

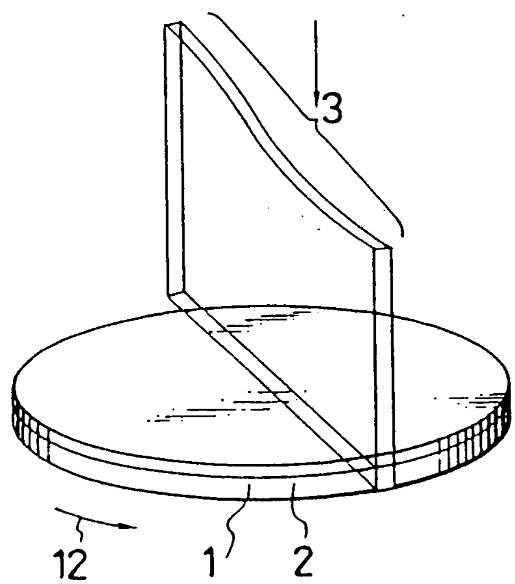

FIG.7

$Bi_2Sr_3Ca_2Cu_2O_x$

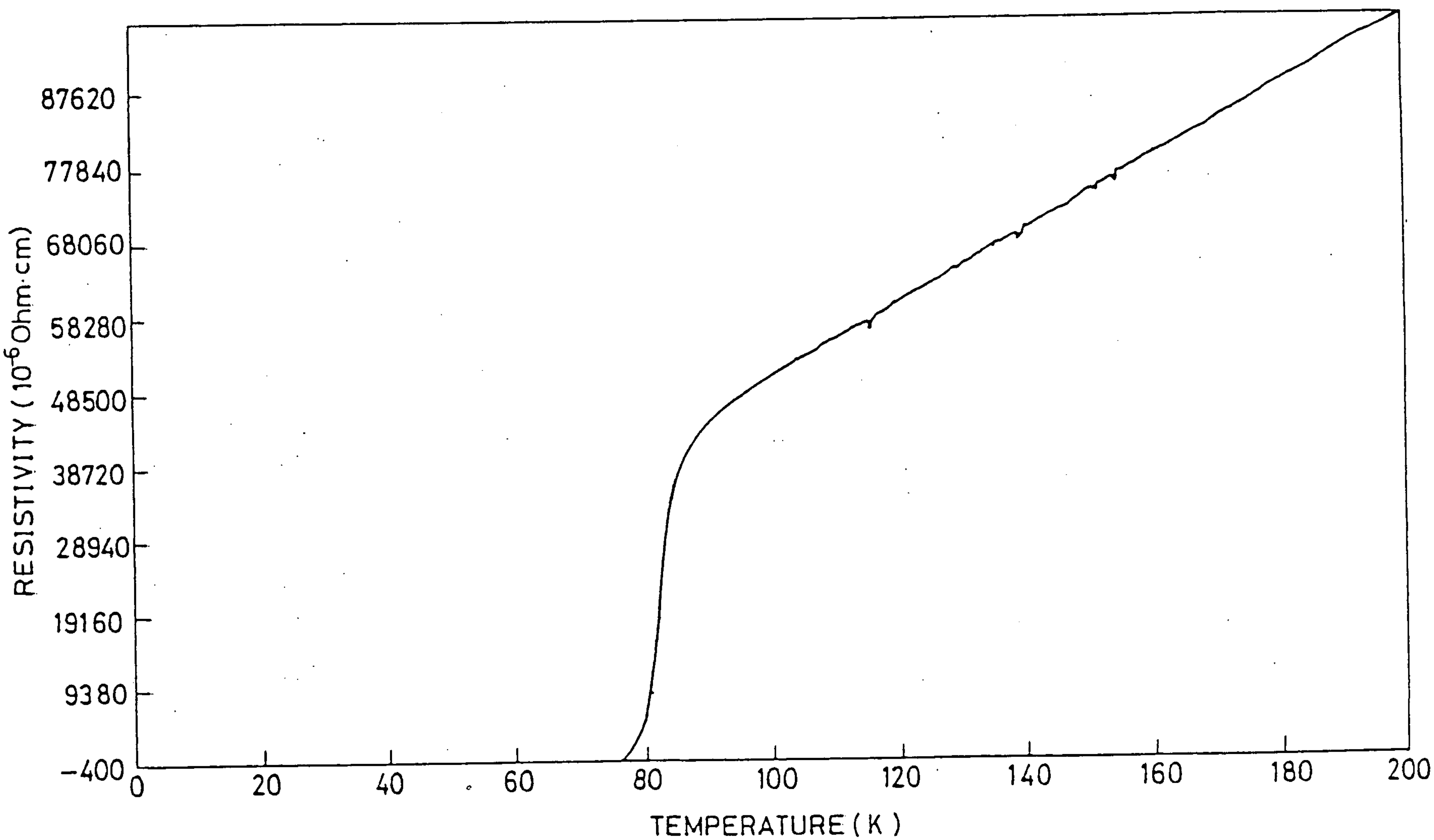

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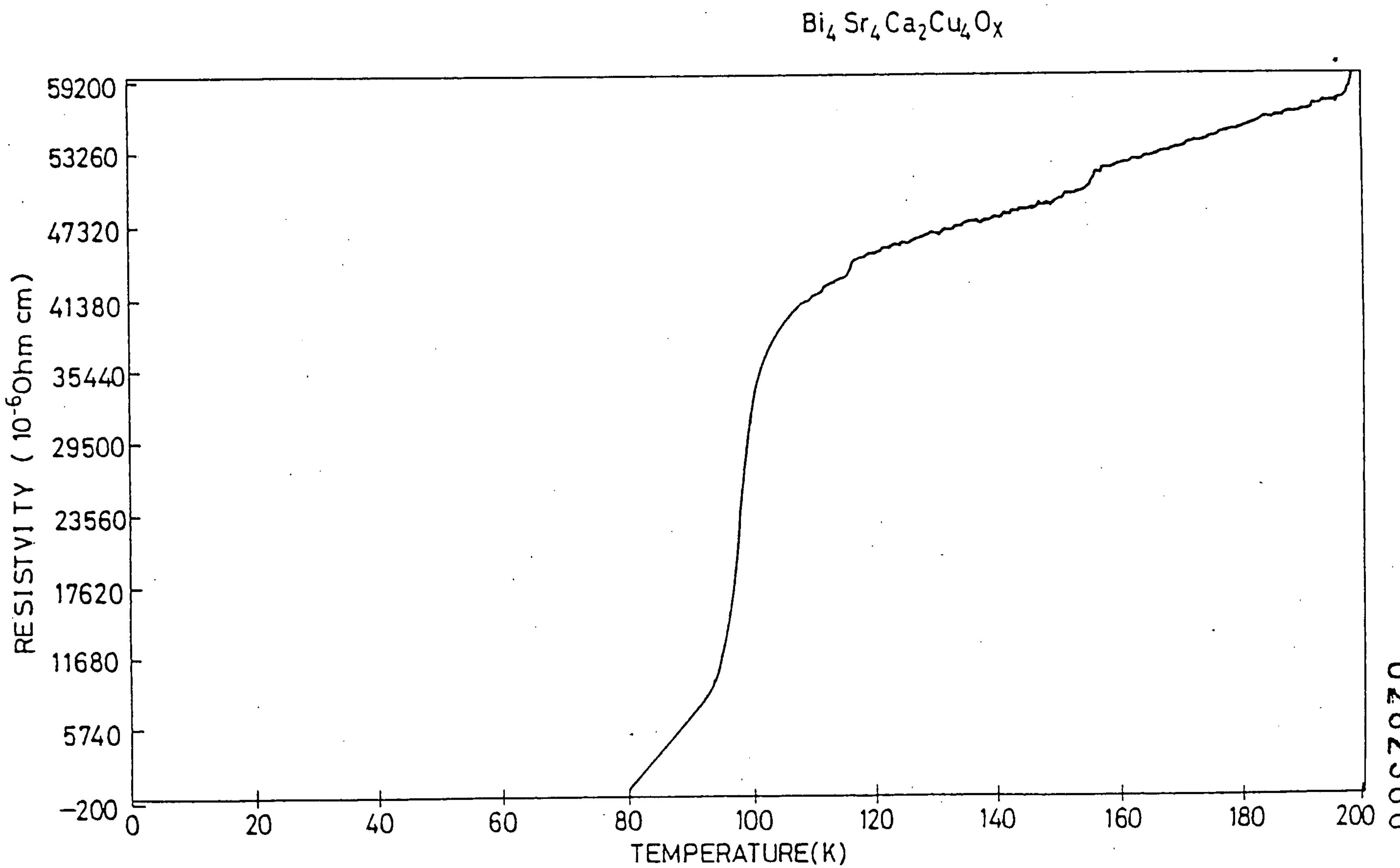
FIG.8



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